



47 Building November 1, 2005

George W. Bruchmann, Chief Waste and Hazardous Materials Division State of Michigan Department of Environmental Quality Constitution Hall 525 West Allegan Street Lansing, MI 48909-7741

RE: Submittal of Midland Representative Soils Sampling and Analysis Plan In Support of Bioavailability Study

George,

In the October 14, 2005 letter transmitting the revised Scope of Work (SOW) for conducting a Remedial Investigation (RI) of Midland Area Soils, The Dow Chemical Company (Dow) committed to provide to the Michigan Department of Environmental Quality (MDEQ) a draft soil sampling work plan for identifying which soil classes are representative of physical and geochemical conditions in surface soils in the City of Midland, Michigan in advance of the RI work plan due on December 31, 2005. The determination of what soil classes are representative of the City, based on the sampling of soil, can be used to support a study to evaluate the effects of physical and geochemical parameters on bioavailability of dioxins and furans from soils. Dow indicated that this soil sampling plan would also describe how a subset of the soil samples will be analyzed for dioxins and furans as well as other chemicals and so provide an initial screening for potential constituents of interest (PCOIs), including dioxins and furans, in advance of the Remedial Investigation which will address PCOIs.

In fulfillment of that commitment, the attached work plan is being provided for your review. Dow intends to commence implementation of the work plan upon approval by the MDEQ. We appreciate the efforts by you and the MDEQ staff to meet and discuss the proposed plan on October 27 and 31, 2005. The attached plan has been revised to incorporate, comments and suggestions provided by the MDEQ and EPA. However, with the expedited timeframe that was selected for submittal, we anticipate that additional dialog will need to occur.

We would appreciate an opportunity to provide clarification or discuss additional questions that are identified during your review of this draft work plan. Please contact me or David Gustafson at 989-636-2953 if you have questions.

Sincerely,

Ben Baker

Senior Environmental Project Leader

The Dow Chemical Company

Midland, MI 48667

Enclosure

Midland Representative Soils Sampling and Analysis Plan In Support of Bioavailability Study

Prepared for

The Dow Chemical Company

November 2005

CH2MHILL

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A Standard Operating Procedure for Recording and Translating of Confidential Spatial Data from the Midland Bioavailability Study

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Abbreviations and Acronyms

bgs below ground surface

C carbon

Dow The Dow Chemical Company

DQO data quality objective

facility Dow Midland Plant

ft feet

H hydrogen

K_{ow} lipophicity

MDEQ Michigan Department of Environmental Quality

N nitrogen

PCA principal component analysis

PCDD/F polychlorinated dibenzo-p-dioxin/furans

QC quality control

QAPP quality assurance project plan

RDCC residential direct contact criteria

RI remedial investigation

SAP sampling and analysis plan

SOM soil organic matter

SOP standard operating procedure

TEQ Toxic equivalents, used to report the toxicity-weighted masses of mixtures of

dioxins and furans

USDA U.S. Department of Agriculture

USEPA U.S. Environmental Protection Agency

1 Introduction

The Midland Representative Soils Sampling and Analysis Plan was originally designed to develop data to support a bioavailability study. Various physical and geochemical parameters in soil have been reported to influence the bioavailability of dioxins and furans in soil and sediment environments. The primary objectives of this investigation are to:

- a) characterize the distribution of physical and chemical parameters reported to influence bioavailability, and
- b) guide sampling efforts to obtain representative soils for use in a bioavailability study.

Based on MDEQ and USEPA's desire to identify the presence and level of non-dioxin and non-furan potential chemicals of interest (PCOIs) and identify other potential Dow-related risk drivers in the City of Midland, a secondary consideration for this investigation will be a pre-RI evaluation of chemicals that may be related to past operations at the Dow Midland plant. Secondary investigation objectives are to:

- a) develop additional information on spatial distribution and concentration range of dioxins/furans, and
- b) perform a preliminary screen for other possible Dow-related constituents

To augment the existing, limited data on the concentrations and distribution of dioxin and furans within the City of Midland, all of the soil samples collected for soil parameter evaluation will also be analyzed to provide additional information on the spatial distribution and concentration range of dioxins/furans. In addition, a second set of samples will be collected and analyzed for a broad suite of chemicals. The results of this set of analyses will provide preliminary information on other constituents that may be related to historical releases from the facility and which may require further evaluation in the RI and RI-related risk assessment activities.

The final objective of this study will be to maintain confidentiality of private property owners. Samples will be collected and evaluated so that it is not possible to correlate analytical results with specific locations or private properties.

This SAP presents:

- the project approach and sampling program for gathering data
- the basis for the number of samples needed to characterize the distribution of physical and geochemical parameters in soil, sufficient to support a bioavailability study
- the design proposed to collect an initial set of samples that will be used to identify chemicals potentially associated with historic manufacturing operations, and
- the process that will be followed to ensure confidentiality of the property owner.

1.1 Study Location

Figure 1-1 depicts Midland and the surrounding area. The 14,400-acre area depicted in this figure is being studied to assess a representative sample of surface soil conditions in Midland. Although the concentrations of dioxins and furans will be measured at throughout this area, previous studies by USEPA (USEPA 1985) and MDEQ (MDEQ 1997) suggest that elevated concentrations of dioxins and furans in surface soils are most likely to be located in close proximity to, and predominantly north and east from the Dow facility. Soil samples will also be collected in the area northeast and southwest of the Dow plant and analyzed to provide a pre-RI evaluation on the presence of other chemicals.

The boundaries of the study were defined by physical features such as major roads to ensure that the study area is bounded by easy-to- identify features and boundaries. The Midland study area does not include the Tittabawassee River floodplain southeast of the Dow facility. The study area encompasses approximately half of the City of Midland and portions of Midland Township. For the purposes of this study, it was determined that it would be appropriate to exclude large industrial properties, water bodies, the Tittabawassee River floodplain, and major roadways from the area available for potential sampling. The industrial facilities were removed to ensure that this study provides information that is generally representative of the soil types found in the parts of Midland where non-industrial exposure may occur and where the bioavailability data may be used to assess potential risk. The following industrial properties were excluded: Dow Midland Facility, developed portions of the Dow Corning Midland Plant, the Dow Salzburg hazardous waste landfill, and the Midland Cogeneration Venture power plant and cooling ponds. Undeveloped portions of the Dow Corning site were retained as part of the study area. With the removal of these areas, the size of the final study area is approximately 10,500 acres.

1.2 Sampling and Analysis Plan Organization

This SAP is organized as follows:

- Section 1 presents an introduction to the Midland study area and identifies the project objectives.
- Section 2 presents the investigation approaches and designs.
- Section 3 describes the methods to be used in evaluating the data to identify soils that are representative of physical and geochemical parameters in Midland soils as well as how results of chemical analyses will be evaluated.
- Section 4 describes the data validation and management procedures.
- Section 5 identifies relevant health and safety plan information.
- Section 6 provides a schedule for the work described in this SAP.
- Section 7 lists references cited in this SAP.

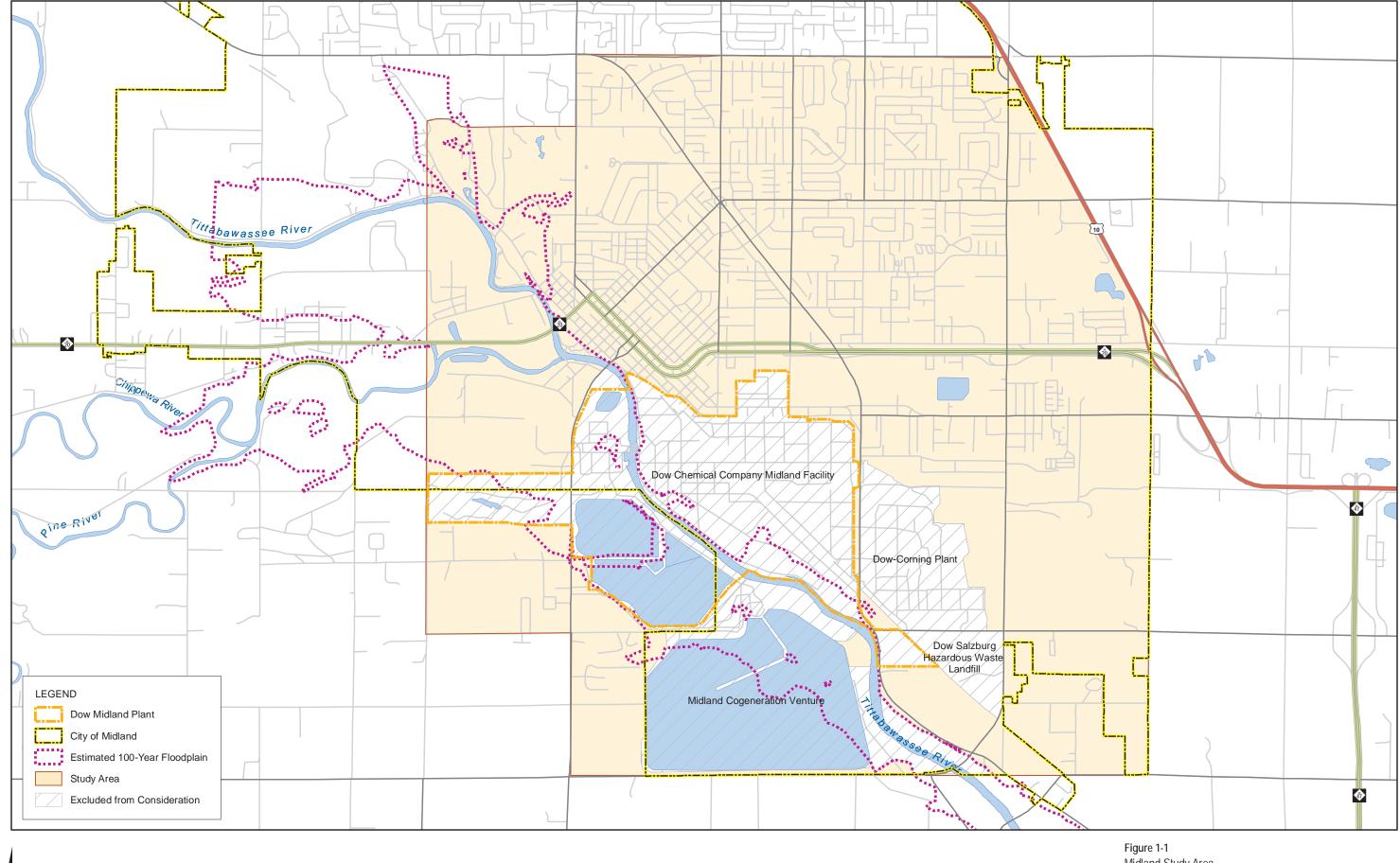


Figure 1-1
Midland Study Area
Midland SAP in Support of Bioavailability Study
Dow Midland Offsite Corrective Actions Program

2 Investigation Approach and Sampling Design

This section describes the data quality objective (DQO) used to develop the sampling design, and the overall approach for characterizing the distribution of physical and geochemical parameters in Midland soils. The approach for collecting samples to provide additional information on the distribution and concentrations of dioxins and furans, and the presence and level of a broader suite of chemicals is also described. Finally, the steps that will be followed to maintain confidentiality of private property owners is presented.

2.1 Data Quality Objective for Characterizing Soil Parameters

As noted in Section 1, the primary objective of this investigation is to characterize soil parameters. This will be done by collecting samples from within the city of Midland and measure each sample for the physical/geochemical parameters that may impact the biological availability of hydrophobic organic soil contaminants. These samples will be evaluated in order to group soils within the study area with respect to these physical/geochemical parameters. The results of this investigation will be used to identify locations within the city from which soil samples will be collected for use in future studies designed to measure bioavailability. The following problem statement has been developed with respect to establishing the DQO for the Midland soils study:

• What relationships, if any, exist between the different physical and geochemical parameters which have been reported to influence bioavailability such that representative soil groups can be identified within the sample area?

2.2 Investigation Approach for Characterizing Soil Parameters

A systematic random sampling approach will be used to identify representative soils within the study area. This approach consists of the following data gathering and evaluation steps:

- 1. Identify the physical/geochemical soil parameters of interest and estimate, from the literature, the expected range of each
- 2. Collect appropriate numbers of samples for characterization of soil parameters.
- 3. Analyze data and define representative groups of soils based on parameters and ranges established in Step 1, and results of tests on samples collected in Step 2.

The following subsections provide the relevant information, evaluation considerations, and decisions that will guide the design of this study.

2.2.1 Physical and Geochemical Influences on Bioavailability

Studies to date have shown that the bioavailability of hydrophobic organic chemicals such as polychlorinated dibenzo-p-dioxins (PCDD)/polychlorinated dibenzo-p-furans (PCDFs) in soil is highly variable, depending not only on a chemical's lipophilicity (K_{ow}), but also

molecular steric conformation and sediment or soil characteristics. The following primary soil parameters been reported to impact the bioacessibility/bioavailability of dioxin and furans (Qiu and Davis, 2004):

- <u>Soil Organic Matter (SOM)</u>: SOM has a strong affinity for most organic compounds and may exist in "rubbery" and "glassy" phases. SOM retards sorption and desorption by its viscosity and by the presence of internal nanopores, which detain molecules and may sterically inhibit their migration and thus limit their bioavailability (Pignatello, 2000). The inherent heterogeneity of SOM results in a wide range of sorption capacity for hydrophobic organic chemicals (HOCs) and nonlinear partitioning behavior in soils and sediments (Gustafsson et al. 1997). Subdomains of SOM include soil organic carbon and black carbon.
- <u>Soil Organic Carbon (SOC)</u>: SOC is a sub-domain of SOM and is a measure of the sorption capacity of a soil for HOCs.
- Specific Surface Area: Surface area has been reported to be a significant factor affecting the bioavailability of PCDD/Fs. A large surface area and high aromaticity enables the formation of π-π interactions (Lyytikäinen et al., 2003). These factors favor stronger binding to soil and sediment, thus decreasing desorption and bioavailability of the chemical. In general, surface area is related to particle size (e.g., smaller particle size generally correlates to a larger specific surface area).
- <u>Particle size</u>: Particle size has been reported to be significant factor affecting the bioavailability of PCDD/Fs. As noted above, particle size is related to specific surface area, with smaller soil particle sizes favoring stronger binding to soil and thus decreasing desorption and bioavailability.
- <u>Hydrogen/Carbon/Nitrogen (H/C/N)</u>: The H/C ratio is a measure of the aromacity of a soil. Increasing H/C levels favor stronger binding to soil and sediment, and thus decreasing desorption and bioavailability of the chemical.
- Black Carbon (BC): BC, a subdomain of SOM, has much higher affinity to planar HOCs than amorphous organic carbon, and has been found to be the predominant repository of many HOCs. BC particles that have sizes ranging from a few microns to above 100 micrometers (µm) are highly aromatic in structure and exhibit relatively low oxygen to organic carbon (O/C) and H/C atomic ratios and low contents of oxygen-containing functional groups (Song et al., 2002). Comparable to diagenetically aged coal, shale and cenospheres, BC also has a high C/O ratio and is responsible for strong HOC sorption (and limited bioavailability) because of its high specific surface areas and relatively reduced chemical nature. It has been proposed that the BC and possibly other distinct subfractions of bulk organic carbon can influence the bioavailability of HOCs (Bucheli and Gustafsson 2001).

The parameters that will be analyzed as part of this study and the concentrations and levels of the parameters that affect bioavailability are listed in Table 2-1. In addition, samples will be collected from each grid node and analyzed for dioxins and furans.

2.2.2 Sample Quantities and Locations

The objective of this portion of this study is to identify groups of samples based on the range of values determined for the physical/geochemical parameters of interest. To accomplish this, an appropriate numbers of samples for the study area and for each potential soil group will be used to support the statistical measures of representativeness. Because nothing is known about the distribution of the physical/geochemical parameters of interest in Midland soil, a sample count based on the 95th quantile with an 85 percent confidence level was selected for use in the study design. As depicted in Figure 2-1, the United State Department Agriculture (USDA) has identified seven different soil classes within the study area. It is not know what relationship, if any, there might be between these soil classes and the physical/geochemical soil properties on interest but for the purposes of designing this investigation, it was assumed that such a relationship might exist. This would mean that seven potential soil groups could be present within the study area. In other words, as many as seven statistically derived groups could be representative of the variation in the parameters affecting bioavailability. The actual number of groups may be more or less than seven. Until samples are collected and analyzed, the number of soil groups is unknown. To achieve the desired confidence level (85%), 35 samples from each statistically determined group will be collected. Assuming that up to 7 such groups may be present, a total 245 samples will be targeted to be collected (7 possible soil groups X 35 samples). A regularly spaced sampling grid deployed across the 10,500 acre study area will be used to identify and characterize the statistically distinct soil groups.

This sample design assumes that access will be granted to all proposed sample locations. This may not occur. The impact that a reduction in the total number of samples would have on the degree of confidence in the results will largely depend on how variable the soil parameters are. If the soil parameters are fairly uniformly distributed within the samples collected, the impact in overall confidence and ability to interpret the results will likely be minimal. If the results suggest that these parameters are much more uneven in distribution, a reduction in the number of samples may have an impact on the overall confidence in the evaluation of the data. However, it will still be possible to use the reduced numbers of samples to identify the present/absence of soil groups with respect to the physical/geochemical parameters.

2.3 Sampling Design for Characterization of Soil Parameters

A sample design has been established to obtain data to meet the data quality objective identified in Section 2.1 for soil properties known to influence bioavailability of hydrophobic chemicals. The sampling design to investigate statistical distribution of physical/geochemical parameters in Midland soils is based on a systematic random sampling approach. The design incorporates the levels of statistical confidence required for the study and the potential groups of soils present in the study area.

As discussed in Section 2.2.2, 245 samples are needed to adequately represent parameter levels in the study area. The study area encompasses approximately 10,500 acres of land (or 4.57×10^8 square feet). This results in a grid spacing of approximately 1,370 feet, with each grid cell representing approximately 43 acres (or 1.8×10^6 square feet). Surface soil samples will be collected for soil parameter characterization at each grid node. In addition, samples will also be collected at each grid node location for dioxin and furan analyses.

The distribution of samples at the grid nodes is shown in Figure 2-1, with a resultant sample count of 244 samples (which approximates the 245 samples desired). The layout of the grid was determined randomly using the Microsoft Excel "RAND" function to identify the point of origin and orientation angle of the grid. Efforts will be made to collect the samples at the locations indicated in Figure 2-1. However, if a location is found to be unsuitable due to physical conditions (e.g., a parking lot, soils have been recently disturbed, etc.) or access restrictions, another location within half the distance (685 feet) to the next grid node will be identified and sampled.

2.4 Investigation Approach for Additional Chemicals

Samples will be collected to generate pre-RI information regarding the presence of chemicals in addition to dioxin and furans that may have been present in Midland soils (see Table 2-2). The following grids will be used to collect these samples (see Figure 2-2):

- a. The first grid is proximal to the northern boundary of the Dow plant with 685 feet between grid nodes. This results in approximately 40 sample locations.
- b. The second grid covers the remainder of the area north of the plant with a grid spacing of 2740 feet. This spacing results in the collection of 13 additional samples.
- c. The third grid is located on the southwest of the Dow plant and has a grid spacing of 1370 feet

Samples collected from these locations will analyzed for the chemicals listed in Table 2–2. Samples will be collected from surface soils (0 – 1inch). At a subset (35) of the locations depicted in Figure 2-2, samples will also be collected from 1 – 6inch below ground surface. Samples collected from these 2 depths at these 35 locations will be compared to provide an initial evaluation of potential differences in vertical distribution of detected analytes in soils.

2.5 Sample Management to Maintain Confidentiality

As detailed in Appendix A, a procedure has been developed to ensure that individuals familiar with the sample locations (field team) are unable to determine the measured concentrations of chemicals in the samples (e.g., chemicals listed in Table 2-2) and individuals familiar with the sample results (data analysts) are unable to determine the identity of the sampled locations. This double blinding process consists of two components:

- (1) translation and rotation of sample location coordinates from state plane coordinates to a new coordinate system with a local origin and modified orientation before the data are transferred to the data analysts, and
- (2) addition of "dummy values" by the data analysis team, making all presentations of the sampled area appear as a square grid of data, ensuring that displays of data and/or analysis results cannot be rotated to match with a sample location map. This procedure will allow statistical and spatial data analysis of the data while maintaining confidentiality of sampling results until confidentiality restrictions are lifted.

Coordinate transformation and sample ID keys will be held by a third party, who will assist with back transformation to original IDs and coordinates when requested.

The implementation relies on 3 parties: the field team, the data analysis team, and an independent third party that serves as an interface between the two teams. The field team records sample location in state plane coordinates ("original coordinates") by using a GPS device, and the third party translates these into a new coordinate system ("masked coordinates") using GIS or other methods and translates sample IDs into random IDs to mask the official sample IDs ("laboratory sample IDs"). MDEQ may be present during the field investigation to observe collection of the soil samples but will not collect samples during the investigation. Instead, sufficient sample volume will be collected from each location and shipped to the third party so that a portion of each sample can be split and shipped to a MDEQ designated laboratory for analysis (see Section 2.9).

The following steps lead from sampling to results:

- 1. The field team records coordinates and sample IDs in the field and labels samples as they are taken.
- 2. The independent third party assigns masked coordinates and laboratory sample IDs to each sample and re-labels samples with the laboratory ID (removing the field sample ID).
- 3. The third party sends the samples to the analytical laboratory, and transmits a table of masked coordinates and laboratory sample IDs to the data analyst team.
- 4. The data analysis team adds as many masked coordinates ("expanded grid points") as is required to expand the regular sampling grid and give the study area the apparent shape of a perfect square with uniform sampling location coverage ("expanded grid").
- 5. The data analysis team receives the analytical data from the laboratory referenced with laboratory sample IDs.
- 6. The data analyst team performs necessary data evaluations.
- 7. The data analysis team reports results on displays that include the expanded grid points or interpolated maps over the expanded grid.
- 8. When confidentiality restrictions are lifted, the independent third party decodes sample locations and sample IDs using the coordinate and sample ID keys.

Appendix A provides a detailed Standard Operating Procedure that will be followed to maintain confidentiality.

2.6 Sample Analyses

The soil samples collected at each grid node will be analyzed for the following:

- Soil particle size distribution
- Specific surface area
- Soil Organic Matter (SOM) content
- Soil Organic Carbon (SOC) content
- Black Carbon (BC) content
- Hydrogen/Carbon/Nitrogen (H/C/N) ratio
- Dioxins/Furans

A set of samples collected at the locations indicated in Figure 2-2will be collected and analyzed for the chemicals listed in Table 2-2. The results of these analyses will provide preliminary information on other possible chemical constituents that may be related to historic manufacturing operations and that will be further evaluated in the RI.

2.7 Sampling Procedures

Samples that will be analyzed for dioxins and furans will be collected from the top one inch of soil. Fifteen samples will be collected from a six (6) foot diameter circle. The fifteen samples will be mixed in a bowl and then transferred to sample containers. Samples that will be collected and analyzed for the chemicals listed in Table 2-2 will be collected from two different depths. Samples will be collected from the top one inch of soil at all of the locations shown in Figure 2-2. At a subset of these locations, samples will also be collected from 1 – 6 inch bgs (see Figure 2-2). Like the samples collected for dioxin and furan analyses, 15 samples will be collected from a 6 foot diameter circle, composited and then transferred to appropriate sample containers.

Hand tools such as stainless steel spoons, trowels or other easily cleaned or disposable material will be used to collect all samples. Cleaned or disposable hand tools, bowls, and spoons will be used to transfer the soil sample to appropriate sample containers. The activities associated with the sampling will be documented in field logbooks. Surface conditions at each sample location (e.g., present/absence of grass, trees overhanging the sample location, etc.) will be also documented. The procedures and QC procedures for sampling and field logbook entries are located in the Field Standard Operating Procedures (SOPs) (CH2M HILL, 2004a) and Quality Assurance Project Plan (QAPP) (CH2M HILL, 2004b).

2.8 Sample Containers and Preservation

Analytical methods, sample bottle requirements, preservatives and hold times associated with each analysis are provided in Table 2-3.

2.9 Quality Control (QC)

Field QC samples will be collected as part of this investigation in accordance with Section 2.5 of the QAPP (CH2M HILL 2004b). Field duplicates will be collected at a minimum frequency of 1 per 10 samples.

If MDEQ desires split samples for chemical analysis, this will be accomplished with a double blind component. Twice the necessary volume will be collected from all locations sufficient for all identified analyses. MDEQ will identify the frequency/number of samples desired for splits, and notify the sample team and the independent third party. Following collection, the entire volume will be shipped to the third party and the protocol for assigning Sample IDs as identified in Section 2.5 will be implemented. Once samples are re-labeled, the third party will ship the split samples to laboratories designated by MDEQ. Splits will receive the same sample ID as the normal sample, and split sample analytical results will be delivered to MDEQ. CH2M HILL will provide its analytical results to MDEQ for split sample comparisons in accordance with the License.

2.10 Sample Handling and Chain of Custody

The procedures used for proper packaging, shipping, and documentation of samples being transported from the sample preparation facility to the laboratory for analysis are provided in the "Sample Handling and Shipping Custody Procedures" of the Field SOP (CH2M HILL, 2004a). After samples are labeled and packaged, they will be shipped to the independent third party for re-labeling and subsequent shipment to the laboratories.

Completed chain-of-custody forms will be required for all samples. The chain-of-custody form will contain the following for each sample:

- Identification number
- Date and time
- Description
- Type
- Preservation
- Analyses required

The original chain-of-custody form will accompany the samples sent to the third party. The third party will prepare a second chain-of-custody form for shipment to the laboratory. The forms will remain with the samples at all times.

2.11 Equipment Cleaning

Personal decontamination procedures will be those provided in the *Dow Health, Safety, and Environment Plan* (CH2M HILL, 2004d). Excess sediment, disposable sample handling equipment, and cleaning materials and liquids will be disposed of in accordance with the "Handling and Disposal of Investigative-derived Waste" of the Field SOP (CH2M HILL, 2004a).

TABLE 2-1Soil Physical and Geochemical Parameters of Interest
Midland Representative Soils Sampling and Analysis Plan in Support of Bioavailability Study

Parameter ^a	Estimated Range		
Soil particle size distribution	Not determined, no data set to estimate ranges		
Specific surface area (SA)	Not determined, no data set to estimate ranges		
Soil organic matter content (f _{om}) Soil organic carbon content (f _{oc}) Black carbon content	1 to 35% 0.5 to 15% (approximately 58% of f _{om}) 1 to 20% of the total organic carbon		
Ratio of hydrogen/carbon/nitrogen (H/C/N)	Not determined, no data set to estimate ranges		

Note:

^a Qiu and Davis, 2004

TABLE 2-2 List of Additional Chemicals Midland Representative Soils Sampling and Analysis Plan in Support of Bioavailability Study

Analytes	CAS Number ^a
Acenapthene	83-32-9
Acenaphthylene	208-96-8
Acrylonitrile	107-13-1
Aldrin	309-00-2
Aluminum (Al)	7429-90-5
Anthracene	120-12-7
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Benzene	71-43-2
Benzo(a)pyrene	50-32-8
Benzo(b)fluoranthene	205-99-2
Benzo(ghi)perylene	191-24-2
Benzo(k)fluoranthene	207-08-9
Beryllium (Be)	7440-41-7
alpha-BHC (alphaHexachlorocyclohexane)	319-84-6
beta-BHC (betaHexachlorocyclohexane)	319-85-7
delta-BHC (deltaHexachlorocyclohexane)	319-86-8
gamma-BHC (Lindane)	58-89-9
Bromodichloromethane (Dichlorobromomethane)	75-27-4
Bromoform (Tribromomethane)	75-25-2
p-Bromophenyl phenyl ether	101-55-3
Boron (B)	7440-42-8
Butyl benzyl phthalate	85-68-7
Cadmium (Cd)	7440-43-9
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
a-Chlordane (cis-Chlordane)	5103-71-9
g-Chlordane (trans-Chlordane)	5103-74-2
bis(2-chlorethyl) ether	111-44-4
Chlorobenzene	108-90-7

TABLE 2-2 List of Additional Chemicals Midland Representative Soils Sampling and Analysis Plan in Support of Bioavailability Study

Analytes	CAS Number ^a
Chloroethane	75-00-3
Chloroform	67-66-3
2-Chloronapthalene	91-58-7
2-Chlorophenol	95-57-8
4-Chlorophenyl phenyl ether	7005-72-3
Chromium (Cr)	7440-47-3
Chrysene	218-01-9
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
4,4'-DDD (p,p'-DDD)	72-54-8
4,4'-DDE (p,p'-DDE)	72-55-9
4,4'-DDT (p,p'-DDT)	50-29-3
Di-n-butyl phthalate (Dibutyl phthalate)	84-74-2
Di-n-octyl phthalate	117-84-0
Dibenzofuran	132-64-9
Dibenz(a,h)anthracene	53-70-3
1,2-Dibromo-3-chloropropane	96-12-8
Dibromochloromethane (Chlorodibromomethane)	124-48-1
1,2-Dibromoethane	106-93-4
trans-1,4-Dichloro-2-butene	110-57-6
1,3-Dichlorobenzene	541-73-1
1,2-Dichlorobenzene	95-50-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane (CFC-12)	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
trans-1,2-Dichloroethylene	156-60-5
2,4-Dichlorophenol	120-83-2
1,2-Dichlorpropane	78-87-5
cis-1,3-Dichloropropene (1-Propene, 1,3-dichloro-, (Z)-)	10061-01-5
trans-1,3-Dichloropropene	10061-02-6

2-10

TABLE 2-2 List of Additional Chemicals Midland Representative Soils Sampling and Analysis Plan in Support of Bioavailability Study

Analytes	CAS Number ^a
Dieldrin	60-57-1
Diethyl phthalate	84-66-2
2,4-Dimethylphenol	105-67-9
2,4-Dinitrophenol	51-28-5
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2
Endosulfan I (.alphaEndosulfan)	959-98-8
Endosulfan II (.betaEndosulfan)	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Ethylbenzene	100-41-4
Fluoranthene	206-44-0
Fluorene	86-73-7
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
2-Hexanone	591-78-6
Indeno(1,2,3-cd)pyrene	193-39-5
Iron (Fe)	7439-89-6
Isophorone	78-59-1
Lead (Pb)	7439-92-1
Manganese (Mn)	7439-96-5
Magnesium (Mg)	7439-95-4
Mercury (Hg)	7439-97-6
bis(2-chloroethoxy)Methane	111-91-1
Methoxychlor	72-43-5
Methyl iodide	74-88-4

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TABLE 2-2 List of Additional Chemicals Midland Representative Soils Sampling and Analysis Plan in Support of Bioavailability Study

Analytes	CAS Number ^a
4-Methyl-2-pentanone	108-10-1
Methylene chloride	75-09-2
2-Methylnaphthalene	91-57-6
Mirex	2385-85-5
Naphthalene	91-20-3
Nickel (Ni)	7440-02-0
Nitrobenzene	98-95-3
N-Nitrosodimethylamine	62-75-9
N-Nitrosodiphenylamine	86-30-6
Pentachlorophenol	87-86-5
Phenanthrene	85-01-8
Phenol	108-95-2
bis(2-ethylhexyl) phthalate	117-81-7
Potassium (K)	7440-09-7
Aroclor 1242	53469-21-9
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1248	12672-29-6
Aroclor 1262	37324-23-5
Aroclor 1268	11100-14-4
Pyrene	129-00-0
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Strontium (Sr)	7440-24-6
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2,-Tetrachloroethane	79-34-5
Thallium	7440-28-0

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TABLE 2-2 List of Additional Chemicals Midland Representative Soils Sampling and Analysis Plan in Support of Bioavailability Study

Analytes	CAS Number ^a	
Toluene	108-88-3	
Toxaphene	8001-35-2	
1,2,3-Trichlorobenzene	87-61-6	
1,2,4-Trichlorobenzene	120-82-1	
1,1,1-Trichloroethane	71-55-6	
1,1,2-Trichloroethane	79-00-5	
Trichloroethylene	79-01-6	
Trichlorfluoromethane (CFC-11)	75-69-4	
2,4,5-Trichlorophenol	95-95-4	
2,4,6-Trichlorophenol	88-06-2	
1,2,3-Trichloropropane	96-18-4	
Vanadium	7440-62-2	
Vinyl chloride	75-01-4	
Zinc (Zn)	7440-66-6	

^a CAS Number from USEPA substance registry website (http://www.epa.gov/srs)

TABLE 2-3
Required Analytical Method, Sample Containers, Preservation, and Holding Times
Midland Representative Soils Sampling and Analysis Plan in Support of Bioavailability Study

Analyses	Preparatory/ Analytical Method	Sample Matrix ^a	Container ^b	Preservative ^c	Holding Time ^d
Volatile Organic Compounds	SW-846 5030B/ 8260B	W	40-mL, glass	HCl, pH < 2, cool to 4°C	14 days
	SW-846 5035/8260B	S	5 g–Encore or equivalent sampling technique	Cool 4°C, or NaHSO ₄ ,and Cool 4°C	48 hours from collection to preservation,
			40-mL, glass	Methanol, cool to 4°C	14 days to analysis
Semivolatile Organic Compounds	SW-846 3510C/ 3520C/ 8270C	W	1-L amber glass	Cool 4°C	7/40 days ^e
	SW-846 3550B/ 8270C	S	4-oz glass	Cool 4°C	14/40 days ^f
Organochlorine Pesticides	SW-846 3510C/3520C/	W	1-L amber glass	Cool 4°C	7/40 days ^e
	8081A SW-846 3550B/8081A Cleanup – 3620B	S	4-oz glass	Cool 4°C	14/40 days ^f
Organophosphorous Pesticides	SW-846 3510C/3520C/	W	1-L amber glass	Cool 4°C	7/40 days ^e
	8141A SW-846 3550B/8141A	S	4-oz glass	Cool 4°C	14/40 days ^f
Herbicides	SW-846 3510C/8151A	W	1-L amber glass	Cool 4°C	7/40 days ^e
	SW-846 3550B/8151A	S	4-oz glass	Cool 4°C	14/40 days ^f
Polychlorinated Biphenyls	SW-846 3510C/3520C/8082	W	1-L amber glass	Cool 4°C	7/40 days ^e
	SW-846 3550B/8082 Cleanup – 3665A	S	4-oz glass	Cool 4°C	14/40 days ^f
Dioxins/Furans	SW-846 8290/EPA Method 1613	W S	1-L amber glass 8-oz glass	Cool 4°C Cool 4°C	30/45 days ⁹
Metals (total)	SW-846 3010A/3020A-SW60 10B Series	W	500-mL polyethylene	HNO ₃ , pH < 2 Cool 4°C	6 months
	SW-846 3050-SW6010B /7000 Series	S	2-oz glass	Cool 4°C,	
Mercury	SW-846 7470A	W	500-mL polyethylene	HNO ₃ , pH < 2 Cool 4°C	28 days
Cyanide	SW-846 7471A SW-846 9010B/9012A	S W	2-oz glass 1-L polyethylene	Cool 4°C, pH>12 NaOH Ascorbic Acid as needed (.6g)	14 days
		S	4-oz glass	Cool 4°C	
Total Organic Carbon	EPA 415.1/SW-846	W	250-mL glass	H₂SO₄ or HCl pH	28 days

TABLE 2-3
Required Analytical Method, Sample Containers, Preservation, and Holding Times
Midland Representative Soils Sampling and Analysis Plan in Support of Bioavailability Study

Analyses	Preparatory/ Analytical Method	Sample Matrix ^a	Container ^b	Preservative ^c	Holding Time ^d
(TOC)	9060	S	2-oz glass	< 2, Cool 4°C Cool 4°C	29 daya
		3			28 days
Percent Moisture	EPA 160.3/ASTM D2216	S	2-oz glass	None	NA
Particle Size Analysis	ASTM D422	S	8-oz glass	None	NA
Soil particle size distribution	ASTM D422 Size separation (sieve) ^h	S	4-oz glass	<10° C	NA
Specific surface area (SA)	BET nitrogen gas physisorption (static pressure technique) ⁱ	S	4-oz glass	<10° C	NA
Soil organic matter content	Loss by ignition ⁱ	S	4-oz glass	<10° C	NA
(f _{om}) Soil organic carbon content (f _{oc})	Combustion	S	4-oz glass	<10° C	NA
Black carbon content	Combustion ⁱ	S	4-oz glass	<10° C	NA
Ratio of hydrogen/carbon/ nitrogen (H/C/N)	Elemental analyzer ⁱ	S	4-oz glass	<10° C	NA

Notes:

Sample container and volume requirements will be specified by the analytical laboratory performing the tests.

Three times the required volume should be collected for samples designated as MS/MSD samples.

- a Sample matrix: \dot{S} = surface soil, subsurface soil, sediment; \dot{W} = surface water.
- b All containers will be sealed with Teflon®-lined screw caps.
- c All samples will be stored promptly at 4°C in an insulated chest.
- d Holding times are from the time of sample collection.
- e 7 days to extraction for water, 40 days for analysis.
- f 14 days to extraction for soil, 40 days for analysis.
- g 30 days to extraction for water, 45 days for analysis.
- h Dane and Topp, 2002.
- i Brunauer et al., 1938.
- °C = Degrees Centigrade
- NaOH = Sodium hydroxide
- TCLP = Toxicity characteristic leaching procedure
- mL = Milliliter
- g = Gram
- Ľ = Liter
- oz = Ounce

BET -Brunauer-Emmett-Teller

HCI = Hydrochloric acid

HNO3 = Nitric acid

EPA = U.S. Environmental Protection Agency

H2SO4 = Sulfuric acid

ASTM = American Society for Testing and Materials

NA = Not applicable

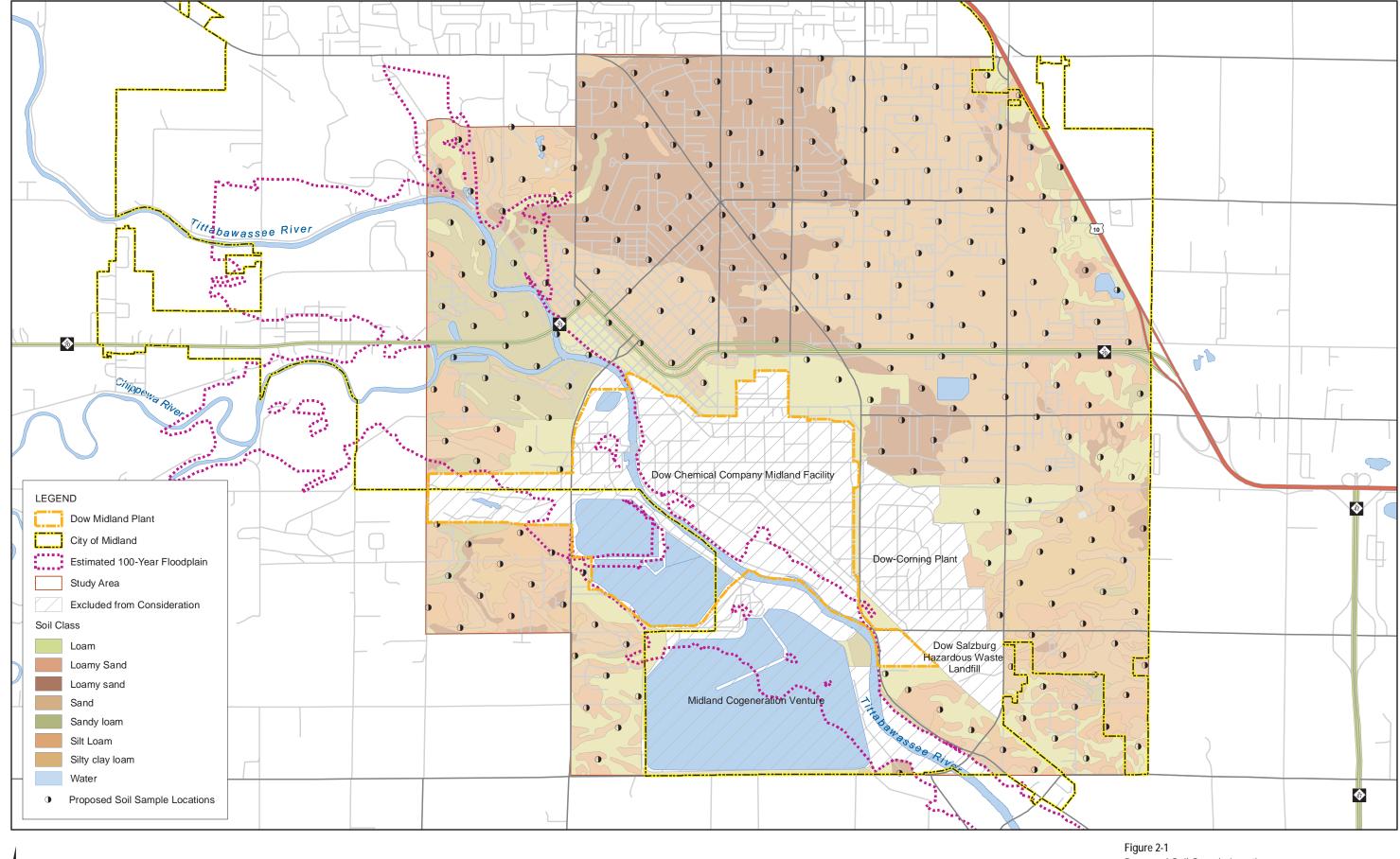


Figure 2-1
Proposed Soil Sample Locations
Midland SAP in Support of Bioavailability Study
Dow Midland Offsite Corrective Actions Program

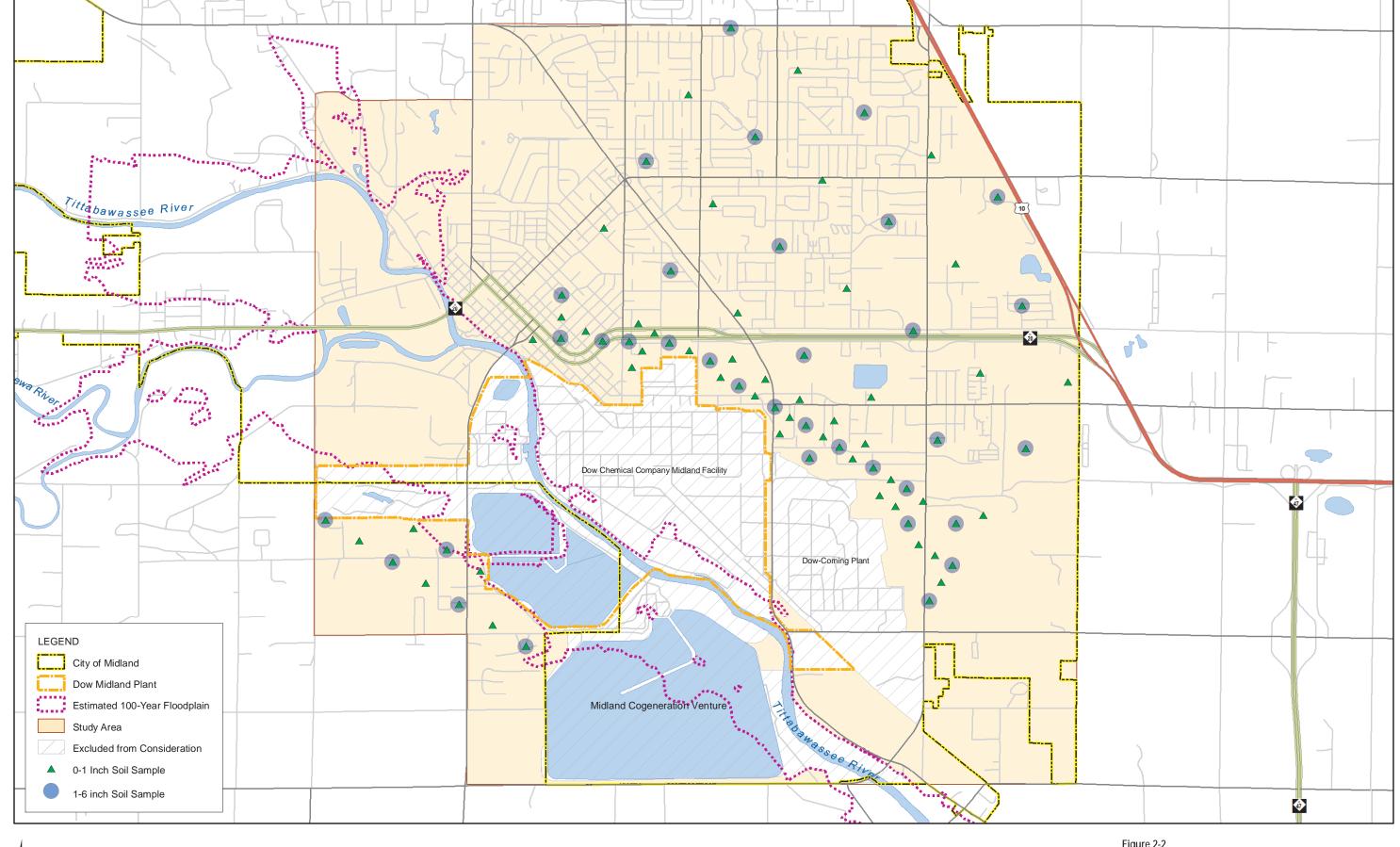


Figure 2-2
Example Sample Locations for Additional Chemicals
Midland Soil SAP in Support of Bioavailability Study
Dow Midland Offsite Corrective Actions Program

3 Data Evaluation

This section of the SAP describes the methods that will be used to evaluate the physical/geochemical soil properties and dioxin/furan analytical results. This section also discusses how the data obtained from the analysis of soil samples for a broad list of chemicals will be used and the limitations associated with these data.

3.1 Evaluation of Soil Parameter Data Results

The quantification of soil physical/geochemical properties potentially influencing bioavailability of dioxins and furans in Midland soils is intended to inform bioavailability work, including the collection of representative soils. Results from these studies, can be used to estimate relative bioavailability of dioxins and furans in study area soils. Representative soil samples from uniformly spaced locations throughout the study area will establish ranges of values for the soil physical/geochemical properties of interest, and provide insight into the spatial distribution of those soil properties within the study area. The analytical results for the samples will be used to calculate best estimates of the ranges of values for each of soil property throughout the study area. This analysis will also provide recommendations as to how materials would best be collected to assure that the soils collected for use in future bioavailability studies represent the soil groups observed within the study area. Meeting the sampling objectives will require both statistical and spatial evaluation of each of the factors potentially affecting bioavailability of dioxins and furans in Midland soils. Data evaluations will be limited to individual soil properties, consisting of the following procedures:

- Statistical distributions for each soil property of interest will be examined through graphical displays (probability plots of observed values against normal and lognormal theoretical values for the sample size). Conventional goodness-of-fit tests (Shapiro-Wilks and/or Shapiro-Francia tests for sample sizes less than and greater than 50 observations, respectively) to establish appropriate methods to estimate ranges of values for the soil properties within the study area will also be applied in the examination of soil properties of interest. Goodness-of-fit distribution test results will determine which equations are appropriate to provide statistical estimates of interest (ranges, median with confidence intervals and/or upper bounds of soil property concentrations).
- Spatial distribution of the soil properties will be performed through plan-view mapping of results throughout the study area. Soil properties exhibiting apparent random distribution of values throughout the area will be considered homogeneous. Soil properties exhibiting localized clusters of elevated or reduced levels will be considered heterogeneous with potentially different subpopulations of concentration levels within the study area. Outputs from the evaluations will include summary statistics of each factor over the study area and the relative homogeneity of each factor and maps supporting application of single or multimodal estimates of factor concentrations. Soil properties exhibiting non-normal behavior and/or spatially clustered results will be evaluated within spatially localized areas to provide more accurate estimates of concentrations within areas exhibiting localized distributions which differ in other areas.

If one or more of the soil properties exhibit multimodal and/or spatially heterogeneous behavior, correlations among soil properties will be evaluated to determine which (if any) soil properties coincide spatially. If soil properties co-vary and exhibit locally different levels of factor concentrations, populations within the study area will be identified as potentially independent areas for collection of soils for use in bioavailability studies.

3.2 Evaluation of Dioxin and Furan Data

As noted in Section 1, existing information on the concentration and distribution of dioxins and furans in the City of Midland is limited. In order to supplement the existing data and to begin to develop a better understanding of the distribution and concentrations of these two chemicals, samples of surface soils will be collected at each of the grid node locations where samples will also be collected to characterize soil parameters. The 244 soil samples analyzed for dioxin and furan will be useful first start in establishing both the statistical and relative spatial distribution of dioxin and furan concentrations in surface soils as follows:

- **Statistical Distribution** The statistical distribution of the results will be evaluated by distribution testing to determine if observed values follow a theoretical normal or lognormal distribution. Point-interval estimates for central tendency and upper bounds will be based upon goodness-of-fit test results.
- **Spatial Distribution** While the true spatial location information is being masked for reasons of confidentiality, the masking has been designed such that geostatistical evaluation of the data is still possible. Consequently, the results can be used to initiate spatial evaluation of dioxin and furan concentrations in the study area. Semivariogram evaluations will be useful to [1] identify directionality of spatial relationships and [2] optimal sample spacing, in the context of the sample spacing represented in the available data. The latter point is important in that the shortest distances from the grid, as designed, is limited to a distance of 1375 feet. Spatial relationships on a smaller scale will not be resolvable from these preliminary data. However, even on this comparatively gross scale, relative concentration orientation will be useful in refining sampling as part of the RI.

The results of this aspect of the investigation will supplement existing information on the concentrations and distributions of dioxins and furans in the city of Midland. The information will be available for use in bioavailability studies, and will be considered during RI evaluations of nature and extent and potential risk.

These data are not intended to be used to evaluate the potential for risk associated with soil contact to the residents within the study area. However, as described in a subsequent section of this document, the results will be evaluated to see if they are above the 1,000 ppt TEQ level that would trigger implementation of an IRA.

3.3 Evaluation of Non-dioxin and Non-furan Constituents Detected in Soil Samples

Data resulting from this portion of the evaluation will provide pre-Remedial Investigation (RI) information on the presence/absence of a broad range of chemicals. This information which

will be supplemented with further sampling, as identified in the RI Work Plan; the RI Work Plan will describe the process that will be followed to collect samples to identify PCOIs characterize nature and extent and complete evaluation of potential risk.

If all proposed samples are collected, the resulting sample set will consist of analytical results from 79 surface samples and 35 subsurface samples from paired locations. This design provides data sufficient to:

- Identify and preliminarily characterize concentration ranges of analytes detected and undetected in Midland surface (0 1 inch) soils (3.3.1);
- Identify and preliminarily characterize concentration ranges of analytes detected and undetected in Midland subsurface (1 6 inches) soils (3.3.2);
- Compare surface and subsurface concentrations of analytes in fixed locations over the Midland Soil site (3.3.3); and
- Estimate the relative efficiency of different spatial configurations of the soil sample collection (3.3.4).

3.3.1 Surface Soil Evaluation (0 – 1 inch)

The initial summary of the analytical results from surface soils will rely upon summary statistics defining:

- counts of detects and samples and resulting frequency of detection [ratio of detect to total counts];
- ranges of reported detects and non-detects; and
- standard summary statistics of mean, median, standard deviation and coefficient of variation.

Resulting tables will be organized to clearly identify presence/absence of analytes occurring in Midland surface soils and establish preliminary point-interval estimates (e.g., mean/median plus confidence intervals) of concentrations.

3.3.2 Subsurface Soil Evaluation (1 – 6 inches)

The initial summary of the analytical results from subsurface soils will rely upon summary statistics defining:

- counts of detects and samples and resulting frequency of detection [ratio of detect to total counts];
- ranges of reported detects and non-detects; and
- standard summary statistics of mean, median, standard deviation and coefficient of variation.

Resulting tables will be organized to clearly identify presence/absence of analytes occurring in Midland subsurface soils and establish preliminary point-interval estimates of concentrations. Given differences in sample sizes [79 surface and 35 shallow subsurface locations]; relative confidence in subsurface concentrations of analytes will be comparatively reduced.

3.3.3 Surface | Subsurface Comparisons

Evaluations of both surface and subsurface soils, independently, will rely upon standard summary statistics, as described in 3.3.1 and 3.3.2. Comparison of the 35 paired surface (0 - 1 inch) and subsurface (1-6 inch) sets of results of analyses for the chemicals listed in Table 2-2 will consist of two steps. First, the pooled set of paired surface and shallow subsurface results will be summarized in the same way. Here, the summary tables will be used to establish which analytes can be reliably compared between the two sample depths. 'Reliability' of comparisons depends, primarily, upon the frequency of detection. Three different cases and applicable evaluation methods are described, as follows:

- 1. The simplest case occurs for the analyte which are detected in all samples. Those analytes will be compared using conventional paired T-tests and/or the nonparametric analogue of the MannWhitney test comparing two populations. Results from the tests will be summarized, listing the analytes for which no statistically significant differences in depths were detected, analytes which were significantly higher in surface samples and analytes which were significantly lower in surface samples.
- 2. The second simple case, which precludes comparisons, consists of analytes for which detection frequencies are zero. Statistical comparisons between concentrations of an analyte detected at the two depths would be meaningless because any differences would simply represent differences in laboratory quantitation.
- 3. The more difficult case includes those analytes for which frequencies of detection lie between 0 and 100 percent. Analytes with extremely low frequencies of detection may be compared strictly on that basis: relative frequency of detection of a given analyte in surface and subsurface samples. Presumably, if there are statistically significant differences in detection frequency, the case would have been made that, to some extent, there are vertical differences in the distribution of the analyte—the substance of the difference can only be evaluated with improved detection limits.

Evaluation results will be summarized in as a list of analytes, grouped by case and statistical test result, defining the case and the presence/absence of statistically significant differences in analyte concentration [case 1] or analyte detection frequency [case 3] in surface and shallow subsurface soils.

3.3.4 Relative Sample Spacing Efficiency

The proposed map of samples distributes shallow subsurface soils more or less uniformly over the three areas targeted for sample collection and analysis on non-dioxin and non-furan analytes at approximately every other node at which a surface sample will be collected. That allocation will result in approximately half the locations with surface [only] and surface plus subsurface results. Statistical comparison using either a paired T-test or nonparametric MannWhitney test would be useful in establishing how consistent results from different locations on the same grid spacing are in characterizing surface soil concentrations of the TAL analytes quantified. If there are no statistically significant differences between the two subsets of surface samples, it can be concluded that the coverage at that spacing is consistent regardless of the specific location of grid nodes. If statistically significant differences occur and occur in localized subsets of the study area, such differences could be used to refine relative sampling density in future sampling efforts.

3.3.5 Use and Limitations of these Data

The results of data collected in this investigation will be sufficient to:

- Provide preliminary information on the presence and level of non-dioxin and non-furan constituents in surface soils in the City of Midland
- compare analytes detected in locations close to the Dow property boundary with locations distant from the Dow property boundary
- give a preliminary indication of whether there are other constituents present at levels that could drive risk evaluations.

The results of this data are not intended to be used to:

- conclude historic manufacturing operations as the source of any analytes detected near the facility boundary
- complete identification of Dow-related PCOIs
- detailed evaluation of potential risk

3.4 Effects of Access Constraints

Implementation of this study and the utility of the data obtained depend on Dow's success in gaining access to the proposed samples locations (shown in Figures 2-1 and 2-2). For sample locations not on Dow-owned property, access agreements will be required from all owners of public and private property. Dow will describe the confidential aspect of the study and indicate that the property owner has the option of obtaining analytical results from any sample collected from their property. Given the potential that access may be denied to a number of properties, Dow will review the access agreements obtained in the context of each sample design prior to initiating these field investigations.

The proposed sampling has been designed to attain data which can characterize physical soil parameters with reasonable confidence over the study area and indicate the presence and level of analytes of interest in Midland soils. Once access efforts have been conducted and completed, potential limitations to the sampling design resulting from lack of access will be evaluated with respect to both number and location of properties giving access. Access constraints on the number of locations granted access may adversely affect the statistical confidence in interpretation of results. Similarly, access constraints, limiting spatial coverage of the study area, could adversely affect the resulting information on the analytes of interest. For example, strictly in terms of sample count, access to 100 properties (of the 245) would have the potential to provide useful statistical estimates. The estimates would achieve a reduced confidence than that planned for, but results could still support preliminary insights into the distribution of the analytes of interest. If, however, the sample of 100 were limited to only a localized portion of Midland, that spatial distribution would greatly affect the representativeness of sample results and limit the area over which conclusions could be reliably applied. Fewer samples over the entire area would increase representativeness but result in reduced confidence in statistical estimates based upon sample results.

If either sample size or spatial distribution or the combination of sample size and distribution appears to severely limit attainment of project objectives, Dow will consider either [1] moving sample locations to properties where access has been obtained or [2] reviewing study objectives and consider adjusting them in the context of the property access that can be achieved. If the potential adjustments still fail to meet the study objectives, Dow will meet with MDEQ to discuss potential alternatives.

3.5 Process for Identifying Sample Locations based on Analytical Results

As discussed above, one of the objectives of this investigation is to maintain confidentiality of property owners. The proposed double-blind procedure will provide that level of confidentiality, but can be "unlocked" if necessary to protect human health. The locations of specific samples will be identified under the following circumstances:

- If any of the samples collected have concentrations of dioxins and furans in excess of 1000 parts per trillion (ppt), Dow will notify MDEQ and send a letter to the independent third party that lists all results > 1000 ppt. The letter will also request that the third party identify the original sample locations and provide these locations to both MDEQ and Dow. Once Dow receives this information from the third party, it will initiate appropriate Interim Response Actions as required for Priority 1 properties in accordance with the Midland IRA.
- These results will be made available prior to initiating the RI if the results of this investigation could alter the RI sample design.
- If other constituents are detected at concentrations greater than 10 times their Part 201 generic cleanup criteria, Dow will meet with MDEQ to discuss the following potential actions:
 - Evaluate results to see if the detection was a single, isolated result or potentially indicative of a broader area which may require additional investigation and discuss scope and timing
 - o Evaluate whether sufficient information exists to determine if an IRA is warranted

4 Data Management and Validation

All data collected under this SAP will be managed in accordance with the QAPP (CH2M HILL, 2004b). However, most of the soil properties specified for this SAP are not standard chemical analyses and do not lend themselves to certain types of QA specified in the QAPP (for example, matrix spikes and method blanks cannot be performed for particle size distribution or black carbon). All analytical results and laboratory reports will be reviewed for accuracy, and validated where feasible. The data will then be accessible for evaluation, interpretation, and reporting activities.

5 Health and Safety

A site-specific amendment to the Dow Health, Safety and Environmental Plan will be prepared for this project and will be approved by the Health and Safety Manager. Prior to beginning sampling work, field team members must read and sign the amendment, and follow its requirements.

6 Schedule

Implementation of this SAP can be affected by the time needed to obtain access to a sufficient number of properties, as well as weather. The schedule shown below has been constructed to identify the key dependencies and timeframes.

- Submittal of Work Plan November 1st, 2005
 - MDEQ Initial Review starting at November 1st submittal
 - Science Advisory Panel Review upon completion of MDEQ review
 - MDEQ Final Review and Approval upon receipt of Science Advisory Panel comments
- Initiate efforts to obtain access Upon MDEQ approval of work plan and sample locations.
- Mobilization of field sampling Upon receipt of access to sufficient properties to
 achieve minimum investigation objectives. Note there are two aspects of access: first
 is receipt of agreements from property owners and second is accessibility to surface
 soils (i.e. no snow cover).
- Field sampling and analytical work
- Submittal of investigation report Within 60 days of completion of sampling, analytical work, data summary and evaluation.

7 References

Brunauer, S., Emmett, P. H., Teller, E. 1938. Adsorption of gases in multimolecular layers. J. Amer. Chem. Soc. <u>60</u>: 309-19.

CH2M HILL. 2004a. Field Standard Operating Procedures. April.

CH2M HILL. 2004b. Quality Assurance Project Plan. April.

CH2M HILL. 2004c. Sample Identification Technical Memorandum. March.

CH2M HILL. 2004d. Dow Health, Safety, and Environment Plan. April.

Dane, J.H., and Topp, G.C., eds. 2002. Methods of Soil Analysis, Part 4, Physical Methods: Madison, WI, Soil Science Society of America, Soil Science Society of America Book Series Number 5.

Michigan Department of Environmental Quality (MDEQ). 2003. *Hazardous Waste Management Facility Operating License for The Dow Chemical Company Midland Plant*. June 12.

Michigan Department of Environmental Quality (MDEQ). 1997. 1996 Midland Area Soil and Sediment Surveys.

Qiu, X. and J. W. Davis. 2004. "Environmental bioavailability of hydrophobic organochlorines in sediments - A review." *Remediation Journal*, Volume 14, Issue 2, pp 55 – 84. March.

United States Department of Agriculture (1979). Soil Survey of Midland County, Michigan.

USEPA. 1985. Study of Dioxin and other Pollutants Midland, Michigan. April 1985.

Appendix A Standard Operating Procedure for Recording and Translating of Confidential Spatial Data from the Midland Bioavailability Study

Standard Operating Procedure for Recording and Translating of Confidential Spatial Data from the Midland Bioavailability Study

Purpose

This operating procedure provides guidelines for the translation of coordinates and sample IDs in order to keep information about the concentration of contaminants on individual properties confidential. The goal is to ensure that individuals familiar with the sampled properties (field team) are unable to determine the measured concentration of chemicals in those samples, and individuals familiar with individual sample results (data analysts) are unable to determine the identity of the sampled properties. This double blinding process consists of two components: (1) translation and rotation of sample location coordinates from state plane coordinates to a new coordinate system with a local origin and modified orientation before the data are transferred to the data analysts, and (2) addition of "dummy values" by the data analysis team, making all presentations of the sampled area appear as a square grid of data, ensuring that displays of data and/or analysis results cannot be rotated to match with a sample location map. This procedure will allow statistical and spatial data analysis while maintaining confidentiality of sampling results until confidentiality restrictions are lifted. Coordinate transformation and sample ID keys will be held by a third party, who will assist with back transformation to original IDs and coordinates when requested.

Scope and Applicability

The implementation relies on 3 parties: the field team, the data analysis team, and a third party (independent contractor) that serves as an interface between the two teams. The field team records sample location in state plane coordinates ("original coordinates") by using a GPS device, and the third party translates these into a new coordinate system ("masked coordinates") using GIS or other methods and translates sample IDs into random IDs to mask the official sample IDs ("laboratory sample IDs"). The following steps lead from sampling to final results:

- 1. The field team records coordinates and sample IDs in the field and labels samples as they are taken.
- 2. The independent contractor assigns masked coordinates and laboratory sample IDs to each sample and relabels samples with the laboratory ID (removing the field sample ID).
- The independent contractor sends the samples to the analytical laboratory, and transmits a table of masked coordinates and laboratory sample IDs to the data analyst team.
- 4. The data analysis team adds as many masked coordinates ("expanded grid points") as is required to expand the regular sampling grid and give the study area the apparent shape of a perfect square with uniform sampling location coverage ("expanded grid").
- 5. The data analysis team receives the analytical data from the laboratory referenced with laboratory sample IDs.
- 6. The data analyst team performs necessary data evaluations.
- 7. The data analysis team reports results on displays that include the expanded grid points or

- interpolated maps over the expanded grid.
- 8. When confidentiality restrictions are lifted, the independent contractor decodes sample locations and sample IDs using the coordinate and sample ID keys.

Field Sample Labeling Procedure (Field Team)

- Record field sample ID, and coordinates (easting, northing in state plane coordinates) in a GPS device. Also record geographic information: land use, vegetation, soil type (soil type information over study area is available in the Sampling and Analysis Plan).
- When labeling sample bottles, each sample bottle should have a separate, removable label containing only the field sample ID. All other label information should be contained on a permanent second label.
- Send samples to the independent contractor for relabeling.
- Transmit table of field sample IDs, coordinates and geographic information to independent contractor for masking.

Coordinate Masking Procedure (Independent Contractor)

- Generate a sequence of random numbers between 1 and the total number of sample IDs. These are the laboratory sample IDs.
- In the order generated, assign each random number to a sample and record a table of Field Sample ID and Laboratory Sample ID (Sample ID Key), relabel sample bottles with laboratory Sample ID and remove Field Sample ID label. Send samples to laboratory.
- Generate two random numbers, one between the minimum and maximum easting, and another between the minimum and maximum northing.
- To mask coordinates, subtract the random easting from each sample easting and the random northing from each sample northing, the result is intermediate X and Y coordinates.
- Draw a random number between 1 and 360, and rotate the intermediate coordinate system clockwise by an angle corresponding to the random number.
- Recalculate the masked coordinates based on the subtraction and rotation.
- Make a table of Masked X, Masked Y, Laboratory Sample ID (Coordinate Key).
- Transmit the table of Masked X, Masked Y, Laboratory Sample ID, and geographic information to the data analysis team.

Grid Expansion Procedure (Data Analysis Team)

- Map the masked sample coordinates in GIS.
- Draw a square around the sample locations.
- Assign dummy points to all locations within the square where no sample points are present

using the same sample spacing as that of the actual sample points.

- When the sample data become available, assign a dummy concentration to each dummy point by simple extrapolation of measured concentrations. This will ensure that dummy points will not stand out as visually different from actual data when data displays are generated.
- For spatial analysis, exclude dummy points, but include them in all visual displays.